

OPIC
OFFICE DE LA PROPRIÉTÉ
INTELLECTUELLE DU CANADA



Ottawa Hull K1A 0C9

CIPO
CANADIAN INTELLECTUAL
PROPERTY OFFICE

(21) (A1)	2,153,372
(22)	1995/07/06
(43)	1996/01/09

(51) Int.Cl. ⁶ C04B 18/12; C04B 18/14; C04B 14/00

(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Zeolite-Hydraulic Cement Containment Medium

(72) Brown, Patrick M. - U.S.A. ;
Maginnis, Michael A. - U.S.A. ;
Furlong, Casey R. - U.S.A. ;
Bakker, Martin G. - U.S.A. ;
Turner, Gregory L. - U.S.A. ;

(71) Same as inventor

(30) (US) 08/272,070 1994/07/08

(57) 13 Claims

Notice: This application is as filed and may therefore contain an incomplete specification.



Industrie Canada Industry Canada

OPIC - CIPO 191

Canada

2153372

ABSTRACT OF THE INVENTION

A zeolite-hydraulic cement containment medium for mining and mineral processing waste material comprising: a hydrated zeolite and a hydraulic cement in a volume ratio of zeolite to cement of from about 1:9 to about 1.1, in which the containment medium is in the form of a monolith and contains less than 50% by volume of the mining or mineral processing waste material.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A zeolite-hydraulic cement containing medium for mining and mineral processing waste material containing an oxy-anion comprising: a hydrated zeolite and a hydraulic cement in a volume ratio of zeolite to cement of from about 1:9 to about 1:1, said containment medium being in the form of a monolith and containing less than 50% by volume of said mining or mineral processing waste material.
2. The zeolite-hydraulic cement containment medium of claim 1, wherein the mining or mineral processing waste material is present in an amount of about 30% by volume of the monolith.
3. The zeolite-hydraulic cement containment medium of Claim 1 wherein said hydraulic cement is portland cement type 1.
4. The zeolite-hydraulic cement containment medium of claim 1, wherein said waste contains an arsenic oxy-anion from refining waste of copper, lead, cobalt, and gold ores.
5. The zeolite-hydraulic cement containment medium of Claim 1, wherein the zeolite is a hydrated $\text{Na}-(\text{SiAlO}_2)$ zeolite containing $\text{Na}_2:\text{Al}_2\text{O}_3:\text{SiO}_2$ with variable amounts of hydrated water in molar ratios of $1:1:2.8 \pm 0.2$.

6. A process for producing a zeolite-hydraulic cement containment medium for mining and mineral processing waste material containing an oxy-anion comprising: passing particles of said mining or mineral processing waste through a sieve having openings of at least 2.80mm and combining the waste particles with a zeolite to form a waste-zeolite mixture; adding the waste-zeolite mixture to hydraulic cement with mixing; adding water to the mixture of waste-zeolite/hydraulic cement in amounts sufficient to produce a free flowing paste; pouring the paste of waste-zeolite/hydraulic cement into a mold for a sufficient period of time to obtain a zeolite hydraulic-cement monolith; and removing the zeolite-hydraulic containment monolith having said waste material therein from the mold.

7. The method of claim 6, wherein zeolite is present in an amount of from about 5 to about 60 weight percent of said paste, and the amount of hydraulic cement is present in an amount of from about 95 to about 40 weight percent of said paste.

8. The method of claim 7, wherein the amount of water added ranges from about 20 to about 35 weight percent of combined hydraulic cement/waste-zeolite mixture.

9. The method of claim 8, wherein the waste is present in an amount of about 30% by volume of said zeolite-hydraulic cement monolith.

10. The process of claim 9, wherein the zeolite is a hydrated $\text{Na}-(\text{SiAlO}_2)$ and the hydraulic cement is a type 1 portland cement.

11. The method of claim 10, wherein zeolite to cement ratios are from about 1:9 to about 1:1.

12. The method of claim 11, wherein the zeolite contains $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2$ with variable amounts of hydrated water in molar ratios of 1:1:2.8 \pm 0.2.

13. The process of claim 6 wherein said oxy-anion is an oxy-anion of arsenic.

ZEOLITE-HYDRAULIC CEMENT CONTAINMENT MEDIUM**BACKGROUND OF THE INVENTION****1. Field of the Invention**

10 The present invention generally relates to a zeolite-hydraulic cement containment medium for hazardous wastes. In particular, the invention relates to a process for preparing a zeolite-portland cement containment medium from a paste prepared by mixing zeolite in amounts from 5-60 weight percent with portland cement in amounts from 95-40 weight percent until a blend is achieved. Thereafter, a chosen amount of small particle size hazardous wastes material is blended with zeolite to form a wastes-zeolite mixture, which is mixed with portland cement. Water is added with mixing to the waste zeolite/portland cement mixture to produce a free flowing paste, and the paste mass is poured into appropriate molds to form a cement monolith after about 7 days.

20 The zeolite-hydraulic cement containment medium of the invention is not encumbered by the disadvantages attendant to the use of portland cement per se, and is therefore able to contain: (1) high-concentrations and high loading levels of arsenic in the presence of high concentrations of other hazardous elements; (2) high amounts of metal cations which normally make soluble complexes with arsenic in the presence of high arsenic and high metal concentrations;

and (3) arsenic in the presence of cations with which it normally makes soluble complexes, and the arsenic is contained in higher concentrations than is usual in portland cement monoliths.

2. Background of the Invention

Control of pollution is one the main concerns in the environment today, and mining, mineral and metallurgical processing wastes in the U.S. accumulate at the rate of thousand of tons per day, and thereby exposes the environment to great risks of pollution. In the field of inorganic hazardous wastes from mining and mineral processing industries, such as the copper mining and processing industry, it has been found that large amounts of oxy-anion wastes (such as arsenic) cannot be disposed of economically. Further, the most common way to solidify and stabilize mining and mineral processing waste solids and waste sludges is cementation using a hydraulic material.

However, cements and other hydraulic material are the most common media for the solidification-stabilization of hazardous waste, and these containment materials after cementation and disposal (by ocean or land) are accompanied by several disadvantageous aspects in that - salts of manganese, tin, zinc, copper and lead are active in reducing the physical strength of these cements, and anions such as phosphate, iodate, borate, and sulfide retard the setting of these

cements, to the extent that, if sufficient quantities of these anions are present, the cement never hardens. In all of these cases, the ions to be contained leach from the cement matrix to some extent.

There are a number of cement-based processes that use various additives in substantial amounts to aid portland cement in the containment of hazardous substances. A general classification of these cement-based processes is as follows: cement/lime, cement/clay, cement/sorbent, and cement/polymer.

In the cement/lime process, lime is used to elevate the pH of the waste containment system to basic values, typically 8-10 in order to form insoluble oxides, insoluble hydroxides, or insoluble calcium salts. Weaknesses of this system are: (1) Some hazardous materials exist as anions which are soluble as calcium salts; and (2) some hazardous cations form hydroxides or complexes at basic pH ranges which are soluble to some extent.

In the cement/clay process, clays are used to absorb hazardous materials. Weaknesses of this system are: (1) The loading capacities of clays vary with the ion or material being attached (in some cases this loading capacity is quite small); (2) Anions do not adhere well on clays; and (3) The ions or materials are adsorbed or absorbed on clays and not strongly bonded chemically. This means the attached ions or materials

may be washed off the clay under the proper conditions. The clay can therefore act as a chromatography bed.

The cement/sorbent system is similar to the cement/clay system, the difference being that the material used to adsorb the hazardous substance is not clay. Sawdust, for example has been used to adsorb oils prior to encapsulation in concrete. The disadvantages of the cement/sorbent systems are essentially the same as the cement/clay system. Additionally, biodegradation of the sorbent may occur if the sorbent is organic.

Cement/polymer systems usually consist of the polymer acting as a permeation limiting device by filling cement pores with hydrophobic materials, and by microencapsulation of the waste material. Usually, there is no direct reaction between the waste constituents and the polymer, and the system does not actually precipitate, adsorb, detoxify, or destroy the hazardous constituents. Biodegradation of the polymer may occur. Leaching of exposed hazardous constituents may occur if the cement monolith becomes cracked or broken.

Accordingly, in mining and mineral processing industries, such as the copper mining and processing industry, which produces large amounts of oxy-anion wastes, such as arsenic, there is a need to devise means whereby these oxy-anion wastes can be disposed of

economically, as the present way of solidifying and stabilizing mining and mineral processing wastes solids and wastes sludges by cementation is uneconomical.

SUMMARY OF THE INVENTION

One object of the invention is to provide a method for producing a hydraulic containment medium for mining and mineral processing wastes materials that is effective for containment of transition metals, heavy metals, and oxy-anions, such as arsenic.

Another object of the invention is to provide a method for producing a hydraulic containment medium for mineral processing wastes containing arsenic from the refining of copper, lead, cobalt and gold ores.

A yet further object of the invention is to provide a method for producing a hydraulic containment medium for solid wastes or sludges.

In general, the method of the invention utilizes a zeolite-hydraulic cement containment medium for hazardous wastes. The containment medium is prepared by obtaining a zeolite-hydraulic cement paste prepared by mixing from about 5 to 60 weight percent of zeolite containing the waste and 95 to 40 weight percent of hydraulic cement until a blend is obtained. The waste is in small particle sizes [Tyler Mesh No. 7 (i.e. 2.80 mm) or higher]. Thereafter, an amount of water sufficient to produce a free flowing paste is

added to waste-zeolite/hydraulic cement mixture with mixing, and the paste mass is then poured into an appropriate mold. After a sufficient period of time from about 24 hours to 7 days, a cement monolith is formed, and can be removed from the mold as a monolith for disposal.

10 The amount of water added depends upon the characteristics of the waste sample, but may vary between about 20 to about 35% by weight of the combined portland cement plus waste-zeolite mixture. After the paste is poured into the mold, good results are obtained when the temperature is kept at about 25°C - 45°C during a 24 hour to 7 day time period in which the monolith is formed.

DETAILED DESCRIPTION OF THE INVENTION

20 Portland cement by itself has been used for many years in Japan and elsewhere for solidification of wastes having hazardous constituents before ocean disposal; however, portland cement has several disadvantages when considering cementation for land disposal of hazardous wastes. For example, salts of manganese, tin zinc, copper and lead are active in reducing the physical strength of portland cement. Further, the anions of phosphate, iodate, borate, and sulfide retard the setting of portland cement, and if sufficient quantities of these anions are present, the

cement will never harden. (P.L. Bishop, Leaching of Inorganic Hazardous Constituents from Stabilized/Solidified Hazardous Wastes. Hazardous Wastes Hazardous Mater., 5(2): 129-143, 1988; P. Cote, Containment Leaching from Cement-Based Forms Under Acidic Conditions. Ph.D. thesis, McMaster University, Hamilton, Ontario, Canada, 1986; M.J. Cullinane et al., An Assessment of Materials that Interfere with Stabilization/Solidification Processes. Proc. 13th Annual Research Symposium, Cincinnati, OH pp. 64-71, 1987; and R.M. Kondo et al., Influence of inorganic salts on the hydration of tricalcium silicate. J. Appl. Chem. Biotechnol, 27:191, 1977).

10

The zeolite-hydraulic cement containment medium of the invention is an excellent medium for containment of materials having transition metals, heavy metals and oxy-anions, especially oxy-anions or arsenic. Oxy-anions are anions which contain oxygen as one component of the moiety.

20

The zeolite-hydraulic cement containment medium for wastes containing arsenic from the refining of copper, lead, cobalt and gold ores - as well as solid wastes or sludges is prepared by mixing from about 5 to 60% zeolite containing waste with about 95 to 40 weight percent of portland cement until an intimate blend is obtained. The hazardous waste is in small particle sizes [Tyler Mesh 7 (i.e. 2.80 mm) or

higher]. Thereafter, an amount of water sufficient to produce a free flowing paste is added with mixing to produce paste mass of zeolite-waste/portland cement. The paste is poured into appropriate molds and kept there until a cement monolith is formed.

More particularly, the monolith formation is formed as follows: (1) Arsenic waste is passed through a sieve of Tyler mesh size 100 and intimately combined with the desired amount of zeolite. (2) Dry hydraulic cement is added to the waste-zeolite mixture in small portions and intimately mixed until all the required cement is incorporated. (3) Water is added with constant stirring until a soft paste stage is reached. The amount of water added will depend upon sample characteristics, but can vary between about 20 to 35% of the combined portland cement plus waste-zeolite mixture. (4) The paste is poured into molds which are kept at a constant humidity (88% relative humidity) and temperature (40°C) for 7 days at which time the monoliths are removed from the molds.

However, the usefulness of the invention is not confined to the percent relative humidity, curing time, and temperature, or cementitious material or zeolite class mentioned. Any relative humidity, curing time, and temperature suitable for the cementation process of a hydraulic cement and any zeolite will suffice.

A typical artificial zeolite-hydraulic cement containment medium according to the invention is monoliths of arsenic waste materials. The containment medium consist of a hydrated Na (SiAlO_2) type zeolite (faujasite) with a cubic structure similar to sodalite, and type 1 portland cement in volume ratios from 1:9 to 1:1 (zeolite to cement). The zeolite contained molar ratios of $\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:\text{SiO}_2$ with variable amounts of hydrated water present of 1:1:2.8+/-0.2 respectively. However, the usefulness of the invention is not confined to this group and/or structure or either natural or artificial origin, as other zeolites will perform the same function.

10

EXAMPLE 1

Containment of Copper Smelter Waste.

Table 1 contains the chemical analysis of a copper smelter waste with typical high metal and high arsenic contents. These high values make containment of copper smelter waste difficult, and usually require large dilution of the waste product. A containment monolith of this material was made using the procedure described above. The monolith contained 30% by volume of the copper smelter waste. The copper smelter waste in the novel zeolite-portland cement containment medium successfully passed EPA's Toxicity Characteristic Leaching Procedure (TCLP) requirements (see Table 2).

20

Table 1

Copper smelter waste sample analysis

Element	Concentration
Antimony.....mg/kg..	8.87
Arsenic.....pct...	10.7
Barium.....mg/kg..	1400
Cadmium.....mg/kg..	1200
Chromium.....mg/kg..	7.7
Copper.....pct...	7.9
Iron.....mg/kg..	97.1
Lead.....mg/kg..	65
Tin.....mg/kg..	536

Table 2

Copper smelter waste TCLP analysis, mg/kg

Element	Concentration permitted by EPA	Concentration Present
Arsenic	5.0	1.81
Barium	100	<1.00+
Cadmium	1.0	0.03
Chromium	5.0	0.07
Copper*	1.0	0.02
Iron*	.4	<0.05
Lead	5.0	<0.05
Mercury	.2	<0.002
Silver	5.0	<0.01
Tin*	5.0	<0.02

*Drinking water standard.

*Element shown as "<" indicate below detection limit of the analytical method used.

EXAMPLE 2

Containment of Arsenic Acid Production Wastes

Table 3 contains the chemical analysis of an arsenic acid production waste with typical high iron

and high arsenic contents. These high values usually make containment of the waste difficult, because arsenic forms a water soluble complex with ferric iron and iron always disproportionates into ferrous and ferric valence states.

Table 3

Crude arsenic acid production waste sample analysis

Element	Concentration
Arsenic.....pct...	32
Barium.....mg/kg..	308
Cadmium.....mg/kg..	60
Chromium.....mg/kg..	57
Copper.....pct...	84
Iron.....mg/kg..	2.6
Lead.....mg/kg..	399
Mercury.....mg/kg..	79
Silver.....mg/kg..	25
Zinc.....mg/kg..	38

A containment monolith of this arsenic waste material was made using the procedure described above. The monolith contained the waste at a loading of 30% by volume. The crude arsenic acid production waste in the novel zeolite-hydraulic cement containment medium successfully passed EPA's Toxicity Characteristic Leaching Procedure (TCLP) requirements (see Table 4).

Table 4

Crude arsenic acid production waste TCLP analysis,
mg/kg

Element	Concentration permitted by EPA	Concentration Present
Arsenic	5.0	2.09
Barium	100	<1.00
Cadmium	1.0	<0.02
Chromium	5.0	<0.05
Copper*	1.0	<0.02
Iron*	.4	<0.05
Lead	5.0	<0.05
Mercury	0.2	<0.002
Silver	5.0	<0.01
Tin*	5.0	<0.02

*Drinking water standard.

*Element shown as "<" indicate below detection limit of the analytical method used.

EXAMPLE 3

Containment of Very High Level Artificial Waste

Table 5 contains the chemical analysis of an artificial inorganic hazardous waste. The high ion content for each element present, i.e., 5960 mg/kg of mercury in the waste is not typical for hazardous waste materials. These high values were used as a measure of the potential effectiveness of the invention containment medium for EPA listed inorganic hazardous elements. A containment monolith of this material was made using the procedure described above. The monolith contained 30% by volume of the waste. This sample successfully passed EPA's Toxicity Characteristic

Leaching Procedure (TCLP) requirements (see Table 6).
Mercury was contained to below detection limits.

Table 5
Artificial inorganic hazardous waste sample
analysis, mg/kg

Element	Concentration
Arsenic	6310
Barium	6290
Cadmium	4600
Chromium	5670
Copper	5950
Iron	4930
Lead	5260
Mercury	5940
Silver	6040
Zinc	5530

Table 6
Artificial inorganic hazardous waste sample TCLP
analysis, mg/kg

Element	Concentration permitted by EPA	Concentration Present
Arsenic	5.0	0.29
Barium	100	.09
Cadmium	1.0	.07
Chromium	5.0	.04
Copper*	1.0	<0.02
Iron*	0.4	.08
Lead	5.0	.51
Mercury	0.2	<0.002
Silver	5.0	.01
Tin*	5.0	.03

*Drinking water standard.

*Element shown as "<" indicate below detection limit of the analytical method used.

Before the advent of the present artificial zeolite-hydraulic cement containment medium, hydraulic cementation has not been very effective with wastes containing oxy-anions, such as arsenate, selenate, etc., or with soluble oxides or hydroxides.

The containment of oxy-anions in the zeolite need not be limited to the direct accessibility of the anion to normal zeolite binding sites. Any form of faujasite zeolite is usable to contain oxy-anions. Further, any zeolite that contains exchangeable monovalent cations are usable in the context of the invention. Further still, any zeolite that contains divalent or trivalent cations is usable in the context of the invention to bind arsenate or other oxy-anions.

The families of zeolites that are useful in the context of the invention are: faujasite, chabazite, zeolite A, zeolite Rho, zeolite ZK-5, zeolite X, zeolite Y. wilhendersonite, gmelinite, edingtonite, natrolite, tetranatrolite, paranatrolite, mesolite, seolecite, thomsonite, gonnardite, analcime, wairakite, gismondine amicite, garronite, gobbinsite, zeolite NaP-1, laumonitite, merlontite, paulingite, phillipsite, harmotome, yugawaralite, canerinite, erionite, levynite, zeolite 1, zeolite losed, zeolite omega, sodalite, offretite, mazzite, bikitaite, dachiardite, epistilbite, ferricite, zeolite ZSM-5, mordenite, brewsterite, heulandite, clinoptilolite,

stibite, stellerite, barrerite, afghanite, liottite, franzinite, sacrofanite, giuseppettite, svetlozarite, doranite, chiarennite, hsianghualite, lovdarite, wenkite, roggianite, partheite, perlialite, viseite, keoheite, leucite, pollucite, herscheilite, phacolite, leonhardite, wellsite, goosecreekite, cowlesite, zeotypes based on aluminum phosphate, and any zeolites made by modifications of these structures.

10 The foregoing description of the specific embodiments will so fully reveal the general nature of the invention that others can, by applying current knowledge, readily modify and/or adapt for various applications such specific embodiments without departing from the generic concept, and, therefore, such adaptations and modifications should and are intended to be comprehended within the meaning and range of equivalence of the disclosed embodiments. It is to be understood that the phraseology or terminology employed herein is for the purpose of description and
20 not of limitation.